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(54) Title: PROCESS FOR PRODUCING POLYFLUOROACYL COMPOSITIONS (57) Abstract A process is disclosed for preparing polyhaloacyl fluorides such as trifluoroacetyl fluoride and difluoroacetyl fluoride by oxidizing 1-chloro-1,2,2,2-trifluoroethanes and 1,1-dichloro-2,2-difluoroethane, respectively with oxygen.		

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TITLE**PROCESS FOR PRODUCING POLYFLUOROACYL COMPOSITIONS**

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Field of the Invention

The instant invention relates to an oxidative process for producing polyfluoroacyl fluorides, chlorides and free acids thereof. More particularly, the instant invention relates to a process which comprises oxidizing at least one polyfluoroalkyl-substituted dichloro- or chlorofluoro-methane. One aspect of the invention relates to oxidizing 1-chloro-1,2,2,2-tetrafluoroethane, CHClFCF_3 (HCFC-124) to trifluoroacetyl fluoride, CF_3COF (TFAF), as the predominant acetyl product, which may be accompanied by lesser amounts of one or more of trifluoroacetyl chloride (TFAC) and trifluoroacetic acid (TFAA). Another aspect of the invention relates to oxidizing 1,1-dichloro-2,2-difluoroethane, $\text{CHCl}_2\text{CHF}_2$ (HCFC-132a), to form a product stream comprising difluoroacetyl fluoride, CHF_2COF (DFAF), difluoroacetyl chloride (DFAC), and the free acid, CHF_2COOH (DFAA).

The polyfluoroacyl fluorides and chlorides are broadly useful as acylating agents for producing agricultural chemicals, pharmaceuticals, industrial products, among other desirable products. The corresponding carboxylic acids are useful as catalysts, intermediates to acid halides, among other products.

Background Of The Invention

Gotoh et al., U.S. Patent No. 5,041,647, discloses oxidizing 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) with oxygen in the presence of water to trifluoroacetyl chloride (TFAC) accompanied by the free acid (TFAA).

Dittman, U.S. Patent No. 3,833,407 produces TFAC by reacting HCFC-123 with oxygen in the presence of active radiation.

Jacobson, U.S. Patent No. 5,241,113 prepares TFAC by oxidizing HCFC-123 with oxygen over a carbon bed in the absence of water.

Childs, U.S. Patent No. 4,022,824 discloses preparing perfluoro carboxylic acid fluorides by a reaction sequence involving (1) a metathesis reaction between an unfluorinated carboxylic acid and a perfluoroacid fluoride, e.g. trifluoroacetyl fluoride (TFAF), normally prepared by electrofluorinating acetic acid, to obtain the unfluorinated carboxylic acid fluoride, followed by (2) electrofluorinating the acid fluoride product of the metathetical reaction to the desired perfluorocarboxylic acid fluoride.

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5 The disclosure of the previously identified U.S. Patents is hereby incorporated by reference

Cross-Reference to Related Patent

10 The instant invention is related to U.S. Patent No. 5,296,640, which issued on March 22, 1994 in the names of Jacobson and Ely, entitled "Process For Preparing Perhalocyl Chlorides" (corresponding to PCT Publication No. WO94/06742); the disclosure of which is hereby incorporated by reference.

Summary of the Invention

15 This invention provides an oxidative process for preparing polyfluoroacyl fluorides from one or more polyfluoroalkyl substituted chlorofluoromethanes and dichloromethanes.

One aspect of the invention provides perfluoroacyl fluorides and chloroperfluoroacyl fluorides from at least one perfluoroalkyl- and
20 chloroperfluoroalkyl- substituted chlorofluoromethanes.

Another aspect of the invention relates to preparing trifluoroacetyl fluoride from a starting material comprising 1-chloro-1, 2,2,2-tetrafluoroethane.

A further aspect of the invention relates to preparing difluoroacetyl fluoride, among other difluoroacetyl derivatives, from a starting material comprising
25 1,1-dichloro-2,2-difluoroethane.

The invention comprises a process for preparing polyfluoroacyl fluorides having the formula $X(CF_2)_n COF$. The process comprises contacting at least one polyfluoroalkyl dihalomethane having the formula $X(CF_2)_n CHClY$ with a source of oxygen, typically in the substantial absence of water, under conditions
30 effective to produce said acyl fluorides, wherein X is H, Cl or F, n is 1 to 4, usually 1, and Y is Cl or F, with the proviso that when Y is Cl, X is H.

Normally, the temperature and pressure are such that the starting material(s) are at or above the critical point, e.g., the supercritical region.

In some cases X is F and n=1, and the acylfluoride comprises
35 trifluoroacetyl fluoride, CF_3COF (TFAF), which may be accompanied by at least one of trifluoroacetyl chloride CF_3COCl (TFAC), and trifluoroacetic acid, CF_3COOH (TFAA). Normally, TFAF is the predominate product at a selectivity of at least about 50%. For example, this aspect of the invention can produce a product stream comprising at least about 60-70 mole % TFAF, about 5 to 15 mole % TFAC,
40 about 10 to 20 mole % TFAA, about 5 to 10 mole % $(CF_3CFCICFCICF_3)$, and about 1 to 5 mole % $ClC(O)F$.

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5 In some cases X is H and n=1 so that the acyl fluoride produced comprises difluoroacetyl fluoride, CF_2HCOF (DFAF), which may also be accompanied by at least one of difluoroacetyl chloride (DFAC), difluoroacetic acid, CHF_2COOH (DFAA), and HCF_2CCl_3 . Normally, DFAF, DFAC and DFAA when taken together are produced at selectivities corresponding to at least about 50%. For
10 example, this aspect of the invention can produce a product stream comprising about 40 to 70 mole % of at least one perhaloacetyl selected from the group of DFAC, DFAF and DFAA, about 10 to 15 mole % CF_2HCCl_3 , about 4 to 10 mole % phosgene, and the remainder, if any, comprises at least one member from the group of HF, CO_2 and water.

15 By "supercritical region", it is meant that combination of temperature and pressure at which the density and other physical properties of the liquid and vapor phases become identical.

The inventive process is normally practiced in the substantial absence of water. By the term "in the substantial absence of water", it is meant that the
20 amount of water present in the conversion or reaction medium as well as the starting materials is limited to that present in the starting materials, and water that may be produced in situ as a byproduct of the overall oxidation; especially when considering that the organic reactants contain chemically-bound hydrogen. Typically, the medium will contain less than about 100 ppm water. The substantial
25 absence of water can permit the inventive process to be practiced in a manner that minimizes hydrolysis of the starting materials and/or products. It will, however, be appreciated by those skilled in this art that TFAF, TFAC, DFAF, DFAC, among other products that are obtained by the present process, may be further hydrolyzed with water to produce TFAA and DFAA.

30 The instant invention is an improvement in this art in that it avoids the need for a source of active radiation and eliminates the need for water or a catalyst, e.g., conventional processes employed water as a catalyst. Without wishing to be bound by any theory or explanation, it is believed that the presence of water can hydrolyze the instant products to their corresponding acids; such acids typically are
35 not as useful for acylating agents when perhaloacylating amines and alcohols, e.g., to form amides and esters. This invention also provides a method for producing at least one of TFAF, DFAF, and related products in which the product can be separated readily from side products and unreacted starting materials, in a highly pure form, e.g., about 96 to about 99 wt % pure. This method also exhibits
40 increased selectivity and conversion to TFAF without the concomitant formation of substantial amounts of TFAA.

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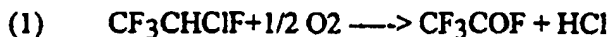
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Detailed Description

The inventive process broadly comprises contacting at least one starting material as defined herein with oxygen at temperatures and pressures and for times effective to produce the desired acyl product(s). An example of the inventive process is exemplified in the following reaction relating to preparing trifluoroacetyl fluoride (equation 1):



Without wishing to be bound by any theory or explanation, it is believed that the presence of CF_3COCl in the product may be accounted for by competitive side reactions (equations 2 and/or 3 below):



It is also believed that the reactions leading to DFAF from $\text{CHF}_2\text{CHCl}_2$ may be the result of the following in situ occurrences:

- (a) Oxidation of HCFC-132a to DFAC, viz.

$$\text{CHF}_2\text{CHCl}_2 + 1/2 \text{O}_2 \longrightarrow \text{CHF}_2\text{COCl} + \text{HCl};$$
- (b) Oxidation decomposition of $\text{CHF}_2\text{CHCl}_2$ or CHF_2COCl to produce HF and H_2O ; and
- (c) reaction of DFAC with HF to form DFAF, viz.

$$\text{CHF}_2\text{COCl} + \text{HF} \longrightarrow \text{CHF}_2\text{COF} + \text{HCl}.$$

The aforementioned DFAF reactions may occur in any expedient sequence. It is further believed that the appearance of DFAA in the product mixture may be explained by in situ hydrolysis of DFAC or DFAF by the H_2O oxidation side product, e.g.,



Examples of other polyfluoroalkyl dihalomethane starting materials (and isomers thereof) and the polyfluoroacyl products that may be prepared therefrom in accordance with the inventive method are tabulated below:

<u>Starting Material</u>	<u>Polyacyl Products</u>
$\text{CClF}_2\text{CHClF}$ (HCFC-123a)	CClF_2COY , Y=F, Cl, OH
$\text{CHF}_2\text{CF}_2\text{CF}_2\text{CHClF}$ (HCFC-235CA)	$\text{CHF}_2\text{CF}_2\text{CF}_2\text{COY}$, Y=F, Cl, OH
$\text{CClF}_2\text{CF}_2\text{CHClF}$ (HCFC-225CB)	$\text{CClF}_2\text{CF}_2\text{COY}$, Y=F, Cl, OH
CHF_2CHClF (HCFC-133)	CHF_2COY , Y=F, Cl, OH
$\text{CF}_3\text{CF}_2\text{CHClF}$ (HCFC-226CA)	$\text{CF}_3\text{CF}_2\text{COY}$, Y=F, Cl, OH

The most significant process parameters for carrying out the reaction are temperature, pressure, and time. Normally, the higher the temperature or pressure, the shorter the time required to achieve an acceptable conversion. The

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5 reaction may be carried out in a temperature range of about 190 to about 320°C, and
at pressures from about 400 to about 2,500 psig. Typically, temperatures of about
190° to 300°C and pressures of about 800 to 2,000 psig are employed. At
temperatures and pressures below the aforementioned range, the conversion rate is
relatively slow. At temperatures greater than those previously identified, the
10 reaction conditions must be controlled to avoid side reactions which can lower the
selectivity to TFAC. Pressures above the previously identified range may be
employed; but the equipment costs would be higher. If desired, the reaction can be
performed at relatively high temperatures by employing much shortened reaction
times. Exemplification of suitable reaction times is provided hereinafter. While the
15 specific reaction time for making a desired product will vary subject to the reaction
variables identified herein, typically the reaction time will be about 10 to about 90
minutes.

While any suitable ratio of oxygen can be employed, normally the
mole ratio of oxygen to the material to be oxidized can range from about 0.1 to
20 about 1, with a ratio of 0.2 to 0.8 being desirable. Oxygen to oxidizable material
ratios above about 1 tend to fall within the explosive range and would not be
preferred. Oxygen to oxidizable material ratios below about 0.5 may reduce the
desired product formation rate such that it becomes desirable to recycle unreacted
starting material. The oxygen is normally diluted with one or more gases, which are
25 inert to the oxidation environment, such as nitrogen, argon, among others, so as to
keep the reaction mixture out of the explosive range and to avoid exotherms which
could decompose the polyfluoroacylfluoride product(s). While any suitable oxygen
source can be employed, molecular oxygen, dried air or mixtures thereof with an
inert gas can be used to practice the invention.

30 A reactor resistant to corrosion by reaction by-products such as
hydrogen fluoride, as well as chlorine and water which can come from the reaction
of byproduct hydrogen chloride and oxygen, is required.

Materials useful for the reactor surfaces include silver, nickel,
tantalum, nickel based alloys sold under the trademarks HASTELLOY®
35 INCONEL® among others. Stainless steel such as 316 is typically unsatisfactory as
it causes many byproducts to be produced, and its use results in decreased
selectivity and conversions. Glass can be severely etched and, therefore, is not
practical. ALLOY C276 sold under the trademark HASTELLOY® 276 and
ALLOY 600 sold under the trademark INCONEL® are the preferred reactor
40 materials since they exhibit minimal corrosion, and selectivity of the desired product
is consistently high.

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5 The acyl fluoride products are isolated by any suitable standard procedure such as distillation. When the product boils below room temperature, the distillation may be carried out under pressure. For example, the purification of TFAF may be achieved by distillation under pressure using a 20 plate Oldershaw column or equivalent. Typically, TFAF is recovered by using a distillation
10 temperature of less than about -60°C whereas TFAC is recovered by using a distillation temperature of less than about -20°C.

 The inventive oxidation process may be carried out either in a batch or continuous fashion. In either case, the process is performed in a manner sufficient to cause the oxygen and raw material to contact and form the desired product. For
15 example, when practicing a continuous process, oxygen and at least one raw material are introduced, for example, simultaneously into a reactor. When practicing a batch process, oxygen is introduced into a reactor containing at least one raw material. In each case conditions, which are not in the explosive range for the mixture of oxygen and the material to be oxidized, are preferred.

20 Depending upon the desired product, the stream exiting the reactor can be recovered as a useful product, separated into its components, at least a portion recycled to the reactor, among other processing steps. An increase in the relative amount of an inert component in the starting material will in turn increase the amount of unconverted material that exits the reactor.

25 While the above description places particular emphasis upon oxidizing certain starting materials, the inventive process can be practiced by using any suitable raw material. Normally, the raw material will be commercially available and about 90 to about 98 % by wt. pure.

30 The following Examples serve to illustrate the invention, but are not intended to limit the scope of the invention.

 All analyses reported in the following Examples were obtained by employing conventional gas chromatography (GC) techniques on a Hewlett-Packard Series II 5890 instrument. A 105 mx0.32 mm RTX-I (Restek Corp., Bellefonte, Pa.) capillary column was used with a thermal conductivity detector for measuring
35 the products and byproducts. A temperature program of 40°C (15 minute hold), heating 16°C/min to 200°C (10 minute hold), and heating 50°C/min to 250°C (10 minute hold) was employed during the Examples.

 "Conversion" and "selectivity" which are used herein are defined as follows. Conversion is the molar % of starting material which was consumed during
40 the inventive oxidation process. Selectivity is defined as:

$$\frac{\text{moles product or byproduct}}{\text{moles starting material consumed}} \times 100\%$$

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Example 1- TFAF

A 400cc Hastelloy® C-276 bomb was charged with approximately 68.2g (0.5 mole) HCFC-124, and perfluorooctane as an internal standard for GC analyses. The bomb was closed and its contents were heated to about 230°C and about 600 psi pressure. Four about 200 psi injections of air from an auxiliary bomb were added at 5 minute intervals. After the final injection, the bomb was heated to a temperature of about 230°C for an additional 15 minutes to give a final pressure of about 1900 psi. The bomb was cooled to approximately -85°C before the air and HCl were vented to a caustic scrubber. The liquid contents were analyzed by gas chromatography using a high pressure syringe for sampling. The analyses indicated about 38% HCFC-124 conversion (95% conversion based on air) to a selectivity of 66% TFAF, 6% TFAC, 16% TFAA, 1% ClC(O)F and 7% (CF₃CFCICFCICF₃).

Example 2 - Difluoroacetyls

20 A 400cc Hastelloy® C-276 bomb was charged with approximately 134.9g (1.0 mole) of HCFC-132a (CF₂HCHCl₂), and carbon tetrachloride as an internal standard for gas chromatography analyses. The bomb was closed and its contents were heated to about 200°C and 450 psi pressure.

Four 100 psi injections of oxygen from an auxiliary bomb were injected at 15 minute intervals to give an approximate one hour reaction time. The bomb was cooled to about -85°C by using dry ice before HCl and any remaining oxygen were vented to a caustic scrubber. The liquid contents remaining in the bomb were analyzed by gas chromatography and showed a 46% HCFC-132a conversion to a selectivity of 15% DFAC, 15% DFAF, 24% DFAA, 13% CF₂HCCl₃, and 6% phosgene. If desired, the product mixture comprising DFAF, DFAC, and DFAA can be hydrolyzed to DFAA by using known technology.

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5 THE FOLLOWING IS CLAIMED:

1. A process for preparing polyfluoroacyl fluorides having the formula $X(CF_2)_nCOF$ comprising contacting at least one polyfluoroalkyldihalomethane having the formula $X(CF_2)_nCHClY$ with an oxygen source to form a mixture, wherein said mixture is exposed to conditions sufficient to obtain said acyl fluorides, wherein X is H, Cl or F, n is 1 to 4, and Y is Cl or F, with the proviso that when Y is Cl X is H.

2. The process of Claim 1 wherein X is F, n is 1 and the acyl product comprises trifluoroacetyl fluoride.

3. The process of Claim 1 wherein X is H and n is 1 and the product comprises difluoroacetyl fluoride, HCF_2COF .

4. A product made by the process of Claim 1 comprising DFAF, DFAC and DFAA.

5. A mixture comprising difluoroacetyl chloride, difluoroacetyl fluoride and difluoroacetic acid.

6. A non-catalytic process for preparing at least one polyfluoroacyl halide having the formula $X(CF_2)_nCOF$ comprising contacting at least one polyfluoroalkyldihalomethane having the formula $X(CF_2)_nCHClY$ with an oxygen source to form a mixture, wherein said mixture is exposed to conditions sufficient to obtain said halide.

7. The process of Claim 1 or 6 wherein said polyfluoroalkyldihalomethane comprises at least one member from the group consisting of $CClF_2CHClF$ (HCFC-123a), $CHF_2CF_2CF_2CHClF$ (HCFC-235CA), $CClF_2CF_2CHClF$ (HCFC-225CB), CHF_2CHClF (HCFC-133), and CF_3CF_2CHClF (HCFC-226CA)

8. The process of Claim 6 wherein said halide comprises at least one member from the group consisting of $CClF_2COY$, Y=F, Cl, OH; $CHF_2CF_2CF_2COY$, Y=F, Cl, OH; $CClF_2CF_2COY$, Y=F, Cl, OH; CHF_2COY , Y=F, Cl, OH; and CF_3CF_2COY , Y=F, Cl, OH

INTERNATIONAL SEARCH REPORT

Internat. J. Application No.
PCT/US 96/03425

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C07C51/58 C07C53/48 C07C53/50		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,5 296 640 (JACOBSON ET AL.) 22 March 1994 cited in the application see claim 1	1
Y	EP,A,0 638 539 (SOLVAY FLUOR UND DERIVATE GMBH) 15 February 1995 see claim 1	1
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" documents member of the same patent family		
Date of the actual completion of the international search 25 June 1996		Date of mailing of the international search report - 5. 07. 96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentplan 2 NL - 2280 HJV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016		Authorized officer Klag, M

INTERNATIONAL SEARCH REPORT

International application No.

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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Lack of technical measures

(Claims searched incompletely: 1)
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

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2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat. Application No.

PCT/US 96/03425

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5296640	22-03-94	EP-A- 0660816 WO-A- 9406742	05-07-95 31-03-94
EP-A-638539	15-02-95	DE-A- 4342601 JP-A- 7053446	16-02-95 28-02-95